DESCRIPTION

MICROPOROUS POLYETHYLENE FILM

TECHNICAL FIELD

The present invention relates to a microporous polyethylene film and a battery separator including the same.

5 BACKGROUND ART

Microporous polyethylene films are now used in various applications such as microfiltration films, battery separators, condenser separators and materials for fuel cells. When used as a battery separator, in

10 particular, as a lithium ion battery separator, a microporous polyethylene film is required to not only have general physical properties such as mechanical strength and permeability, but also excel in "fuse effect" and "heat resistance" so as to secure the

15 safety of the battery.

The mechanism of "fuse effect" in the film as a separator of a battery is such that when the inside of the battery is overheated due to over charge or the like, the separator fuses and forms a film that coats

20 the electrodes to interrupt current flow, thereby ensuring the safety of the battery. It is known that in microporous polyethylene films, their fusing temperature, that is, the temperature at which their

fuse effect develops is around 140°C; but on the other hand, from the viewpoint of stopping the runaway reaction in the inside of batteries as soon as possible, it is considered that the lower the fusing

5 temperature, the better.

Furthermore, considering its function, the shape of the separator has to be maintained even after fusing so as to maintain the electrical insulation between the electrodes. This means that the separator,

10 or microporous polyethylene film is required to excel in "heat resistance", as described above. The "heat resistance" can be considered from two aspects: film rupture properties and heat shrinkable properties. For example, to secure the safety of batteries at 150°C, US

15 Standard, "Standard for Lithium Batteries" UL1642, stipulates a safety evaluation standard for batteries that require batteries to be stored in an oven at 150°C for 10 minutes. To come up to this safety standard, the separator is preferably such that after being made

20 pore-free by fusing, it does not rupture at temperatures of 150°C or higher and undergoes the least possible heat shrinkage, thereby being able to maintain its shape. Any direct contact of the anode and cathode electrodes caused by film rupture or heat shrinkage,

25 particularly heat shrinkage of wound battery body across its width induces a short circuit in the inside of the battery, whereby the battery becomes unsafe. Thus, there is a strong demand for a separator having

excellent heat resistance.

It is important that film-rupture resistance and low heat shrinkability are compatible with each other, and only a separator having excellent film-rupture resistance and low heat shrinkability at the same time deserves being referred to as separator having excellent heat resistance.

A number of microporous films have been developed aiming at securing the safety of batteries, in other words, improving both the fuse effect and the heat resistance of batteries. However, in actuality, disclosed have been only technologies for microporous films excelling in either fuse effect or heat resistance, and thus it has been difficult to provide a microporous polyethylene film that satisfies both the general physical property requirements, such as mechanical strength and permeability, and the safety requirements, such as fuse effect and heat resistance.

For example, a technology for providing heat resistance to a microporous film and lowering the fusing temperature of the same has been known in which ultrahigh molecular weight polyethylene is blended with low molecular weight polyethylene or branched- or linear-low density polyethylene, as described in Patent Documents 1 and 2. This method is expected to provide a microporous film with heat resistance, owing to its ultrahigh molecular weight component, while lowering the fusing temperature of the film to some extent.

However, blending ultrahigh molecular weight polyethylene simply with low molecular weight polyethylene is insufficient to lower the fusing temperature. Further, blending ultrahigh molecular

5 weight polyethylene with branched- or linear-low density polyethylene so as to lower the fusing temperature more effectively makes film rupture likely to occur at the interface between the two types of polyethylene, because ultrahigh molecular polyethylene

10 has a poor affinity for branched- or linear-low density polyethylene resulting in poor film-rupture resistance. Furthermore, increase in the amount of branched- or linear-low density polyethylene added lowers the degree of crystallinity of the film, thereby making it

15 difficult to make the film porous, which poses a problem of affecting the permeability of the film.

There is proposed in Patent Document 3 a microporous polyethylene film produced by blending a specific high molecular weight polyethylene copolymer

20 with high density polyethylene, thereby having a low fusing temperature and a certain degree of film rupture resistance. This microporous polyethylene film, however, still poses a problem of having increased heat shrinkage because it is composed of high molecular

25 weight components alone.

There is proposed in Patent Document 4 a microporous polyethylene film which is composed of high density polyethylene and polyethylene having a specific

melting point, thereby having a lower fusing

temperature. However, it is difficult to allow a

microporous polyethylene film to have mechanical

strength, permeability and heat resistance in a well-

5   balanced manner, while maintaining its low fusing

temperature, by simply adding polyethylene having a

specified melting point, particularly when the film is

made thin.

Patent Document 1: JP-A-2-21559

10   Patent Document 2: JP-A-5-25305

Patent Document 3: JP 3113287 (USP 6168858,

EP 814117B1)

Patent Document 4: JP-A-2002-338730

DISCLOSURE OF THE INVENTION

15   Accordingly, the object of the present

invention is to overcome the above described problems,

thereby providing a microporous polyethylene having

excellent mechanical strength and permeability, and

besides, a low fusing temperature and high heat

20   resistance.

After intensive examination of the amount of

the copolymer contained in polyethylene, the molecular

weight of polyethylene, etc., the present inventors

have found that, surprisingly, a microporous

25   polyethylene film which includes a blend containing

polyethylene copolymer having a specific flowability

and density is superior in balance of mechanical

strength, permeability and heat resistance to conventional microporous polyethylene films that have a low fusing temperature.

Specifically, the present invention is as
5   follows:

(1)   A microporous polyethylene film, including a blend that contains a high density polyethylene copolymer which has a melt index (MI) of 0.1 to 100 and a content of an α-olefin unit with 3 or more carbon
10 atoms of 0.1 to 1% by mole; and high density polyethylene which has a viscosity average molecular weight (Mv) of at least 500000 to 5000000, wherein the blend has an Mv of 300000 to 4000000 and a content of an α-olefin unit with 3 or more carbon atoms of 0.01 to
15 1% by mole.

(2)   A microporous polyethylene film, including a blend that contains a high density polyethylene copolymer which has a melt index (MI) of 0.1 to 100 and a content of an α-olefin unit with 3 or more carbon
20 atoms of 0.1 to 1% by mole; and homopolyethylene which has an Mv of at least 500000 to 5000000, wherein the blend has an Mv of 300000 to 4000000 and has a content of an α-olefin unit with 3 or more carbon atoms of 0.01 to 1% by mole.

25 (3)   A microporous polyethylene film, including a blend that contains a high density polyethylene copolymer containing an α-olefin unit with 3 or more carbon atoms, and a high density polyethylene,

characterized in that the microporous polyethylene film has a weight fraction measured by GPC of a component having a molecular weight of 1000000 or less is 1 to 40%, and a weight fraction measured by GPC of a

5 component having a molecular weight of 10000 or less is 1 to 40%, the component having a molecular weight of 10000 or less has a content of an α-olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole, and the blend has an Mv of 300000 to 4000000, and a content of

10 an α-olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole.

(4)   The microporous polyethylene film according to any one of the above (1) to (3), wherein the above described α-olefin is propylene.

15 (5)   The microporous polyethylene film according to any one of the above (1) to (4), wherein the above described polyethylene having an Mv of 500000 to 5000000 is a blend of two or three kinds selected from the following polyethylenes (A), (B) and (C):

20   (A) the above described polyethylene having an Mv of 1500000 or more and less than 5000000; (B) the above described polyethylene having an Mv of 600000 or more and less than 1500000; and (C) the above described polyethylene having an Mv of 250000 or more and less

25 than 600000.

(6)   The microporous polyethylene film according to any one of the above descriptions (1) to (4), wherein the above described polyethylene having an Mv

of 500000 to 5000000 is an ultrahigh molecular weight polyethylene having an Mv of 1500000 or more.

(7)   The microporous polyethylene film according to any one of the above descriptions (1) to (6), having a film rupture temperature of 150°C or higher.

(8)   The microporous polyethylene film according to any one of the above descriptions (1) to (7), having a shrinkage force at 150°C of 2N or less.

(9)   The microporous polyethylene film according to any one of the above (1) to (8), having a fusing temperature of 140°C or less.

(10)   The microporous polyethylene film according to any one of the above (1) to (9), having a thickness of 5 to 24 μm.

(11)   The microporous polyethylene film according to any one of the above (1) to (10), having a porosity of 30 to 70%.

(12)   The microporous polyethylene film according to any one of the above (1) to (11), having an air permeability of 100 seconds or more and 600 seconds or less.

(13)   A battery separator, including a microporous film according to any one of the above (1) to (12).

The microporous film of the present invention excels in mechanical strength, permeability and productivity and has a low fusing temperature and high heat resistance; and therefore, it is preferable as a battery separator.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A to 1C are views showing a measuring device for measuring the fusing temperature and short-circuit temperature of a film: FIG. 1A is a schematic view; FIG. 1B a plan view of nickel foil 2A; and FIG. 1C a plan view of nickel foil 2B.

BEST MODE FOR CARRYING OUT THE INVENTION

In the following the present invention will be described in detail in terms of its preferred embodiments.

In one embodiment, the microporous film of the present invention includes a blend of a high density polyethylene copolymer; and high density- or homo-polyethylene (hereinafter sometimes referred to simply as "blend").

From the viewpoint of flowability and shrinkage force relaxiation at the time of shutdown and moldability, the melt index (MI) of the high density polyethylene copolymer is 0.1 to 100 and preferably 0.5 to 10. The viscosity average molecular weight (Mv) of the same is 10000 to 250000.

The comonomer of the high density polyethylene copolymer is an α-olefin with 3 or more carbon atoms (hereinafter sometimes referred to simply as "comonomer"), and examples of such comonomers include propylene, butane, pentene, hexane, heptene and octane. From the viewpoint of the affinity for other

types of polyethylene, propylene, which has 3 carbon
atoms, is most preferable of the above comonomers.

The amount of the α-olefin unit with 3 or
more carbon atoms in the high density polyethylene
5   copolymer is 0.1 to 1% by mole and preferably 0.2 to
0.8% by mole per 100% of ethylene unit in the same. If
the amount is less than 0.1% by mole, the effect of
lowering the melting point is not produced, whereas if
the amount is more than 1% by mole, the degree of
10 crystallinity of the resultant film lowers, resulting
in a microporous film of poor permeability.

The density of the high density polyethylene
copolymer needs to be high from the viewpoint of
melting point and permeability, though it is related to
15 the amount of the α-olefin unit with 3 or more carbon
atoms contained in the polyethylene. The term "high
density" herein used means 0.93 to 0.97 and preferably
0.94 to 0.96.

The high density polyethylene copolymer used
20 in the present invention can be produced by various
known processes. For example, it can be produced by
polymerization using catalyst supported by a chromium
compound, Ziegler catalyst containing magnesium
compound or metallocene catalyst as disclosed in JP-B-
25 1-12777.

The polyethylene blended with the high
density polyethylene copolymer (hereinafter sometimes
referred to simply as "polyethylene blended") is

preferably high density polyethylene which contains less than 0.1% of comonomer unit or homopolyethylene which contains no comonomer. The term "high density" herein used may be defined as the same as that used in

5 the above described a high density polyethylene copolymer.

Specifically, the microporous film of the present invention contains, besides the high density polyethylene copolymer, at least any one type of

10 polyethylene selected from the above described types of polyethylene which has an Mv of 500000 to 5000000 and preferably 600000 to 4000000, and it may contain any several types of polyethylene selected from the above described types of polyethylene. The percentage of

15 these types of polyethylene in the blend is preferably 10 to 90%, more preferably 30 to 85% and much more preferably 40 to 80%. Blending two or three types of polyethylene selected from the following types of polyethylene:

20 (A) polyethylene having an Mv of 1500000 or more and less than 5000000,

(B) polyethylene having an Mv of 600000 or more and less than 1500000, and

(C) polyethylene having an Mv of 250000 or more and

25 less than 600000 is particularly preferable, because doing so increases the affinity among the types of polyethylene blended, thereby making it possible to fully draw out the heat resistance, which a high

molecular weight component brings about, and fusing properties, which a high density polyethylene copolymer brings about.

The percentage of the high density polyethylene copolymer in the blend is, from the viewpoint of fusing properties and permeability, preferably 10 to 90%, more preferably 15 to 70% and much more preferably 20 to 60%. If the percentage is lower than 10%, the fusing properties become insufficient, whereas if the percentage is higher than 90%, the heating resistance becomes insufficient.

To further draw out the good fusing properties, which are brought about by the high density polyethylene copolymer, it is preferable that the polyethylene blended is ultrahigh molecular weight polyethylene having an Mv of 1500000 or more.

In this case, the percentage of the high density polyethylene copolymer in the blend is, from the viewpoint of fusing properties and mechanical strength, preferably 10 to 90%, more preferably 30 to 85% and much more preferably 40 to 80%.

The Mv of the blend is, from the viewpoint of mechanical properties, preferably 300000 to 4000000, more preferably 400000 to 3000000 and much more preferably 500000 to 1000000. If the Mv is less than 300000, the heat resistance becomes insufficient, whereas if the Mv is more than 4000000, the viscosity becomes too high, and thus, the moldability becomes

poor. The Mv of the blend in the present invention means the Mv of the blend of raw materials and/or that of the end product.

The amount of the comonomer unit contained in the blend is 0.01 to 1% by mole and preferably 0.1 to 0.8% by mole per 100% of ethylene unit.

Another embodiment of the present invention is a microporous polyethylene film, including a blend that contains a high density polyethylene copolymer containing α-olefin unit with 3 or more carbon atoms; and at least high density polyethylene having an Mv of 500000 to 5000000, characterized in that the weight fraction measured by GPC, of polyethylene having a molecular weight of 1000000 or less is 1 to 40%, that of polyethylene having a molecular weight of 10000 or less is 1 to 40%, the content of the α-olefin unit with 3 or more carbon atoms in the component having a molecular weight of 10000 or less is 0.1 to 1% by mole, the Mv of the blend is 300000 to 4000000 and the content of α-olefin unit with 3 or more carbon atoms is 0.01 to 1% by mole. In such a microporous polyethylene film, the component having a molecular weight of 1000000 or more and the component having a molecular weight of 10000 or less each preferably account for 1 to 40%, more preferably 1 to 30%, and much more preferably 1 to 20%, based on the molecular weight distribution measurement by GPC. If the percentage of each component falls in this range, the balance of the

fusing properties, heat resistance and mechanical strength is further enhanced, which makes strechability of the microporous polyethylene film better. To allow the blend to contain components having such molecular

5   weights, the blend has to contain a high density polyethylene copolymer having an MI of 0.1 to 100 and at least polyethylene having an Mv of 500000 to 5000000.

The blend may contain polyethylene having an

10 Mv higher than that of the high density polyethylene or any other polyolefin, as long as the performance of the blend is not impaired. Examples of such polyolefins include, not limited to, polypropylene, polymethylpentene and polybutene. Of these

15 polyolefins, polyethylene is most preferable.

Then the preferable process for producing a microporous polyethylene film of the present invention will be described.

A microporous polyethylene film is produced

20 by: first dissolving polyethylene in a solvent called plasticizer at temperatures higher than or equal to its melting point of the polyethylene, cooling the resultant solution to temperatures lower than or equal to its crystallization temperature to form polymer gel

25 and using the polymer gel to form a film (film forming step); stretching the resultant film (stretching step); and removing the plasticizer (plasticizer removing step). In this production process, the order of the

stretching step and the plasticizer removing step can
be reversed.

The term "plasticizer" herein used means an
organic compound compatible with polyethylene at
5   temperatures lower than or equal to its boiling point.
Concrete examples of such plasticizers include:
decaline, xylene, dioctyl phthalate, dibutyl phthalate,
stearyl alcohol, oleyl alcohol, decyl alcohol, nonyl
alcohol, diphenyl ether, n-decane, n-dodecane and
10   paraffin oil. Of these plasticizers, paraffin oil,
dioctyl phthalate and decaline are particularly
preferable.

The percentage of the plasticizer in the
polymer gel is, not limited to, preferably 20% to 90%
15   and more preferably 30% to 80%. If the percentage is
less than 20%, a microporous film having a proper
porosity is sometimes hard to obtain, whereas if the
percentage is more than 90%, the viscosity of the
heated solution is lowered, which sometimes makes hard
20   the continuous molding of the polymer gel into a sheet.

In the following the process for producing a
microporous polyethylene film will be described in
terms of the above described three steps that
constitute the process: film forming step; stretching
25   step; and plasticizer removing step.

Film Forming Step

The process for forming a film is not limited
to any specific one. A sheet having a thickness of

several tens μm to several mm can be continuously formed by: for example, feeding mixed polyethylene powder and a plasticizer to an extruder; melt kneading both of the above materials at around 200°C; and casting

5   the kneaded materials from an ordinary coat-hanger die to a cooling roll. The known inflation method may also be used. The method for feeding a raw material and a plasticizer in the above described process may be any known method in which resin and a plasticizer are fed

10 in the completely solved state or in the slurry state. From the viewpoint of productivity, it is preferable to feed resin from a feed hopper and a plasticizer halfway to an extruder. In this case, the extruder may be provided with more than one feed opening for feeding a

15 plasticizer.

In the above described process, powdered polyethylene having an average particle size of 1 to 150 μm is preferably used because the use of such polyethylene makes the melt kneading operation more

20 efficient. Particularly when using ultrahigh molecular weight polyethylene having a Mv as high as or higher than 1500000, the average particle size of the polyethylene is preferably 1 to 150 μm, more preferably 1 to 100 μm and particularly preferably 1 to 50 μm.

25 Such powdery polyethylene, whose particle size is smaller than usual ones, may be prepared by sizing with a sieve or the like or can be produced by properly selecting a catalyst etc. in the step of

polymerization.

Stretching Step

Then, the resultant sheet is stretched at least mono axially to form a stretched film. Examples

5 of stretching methods applicable include: not limited to, tentering, rolling and rolling. Of these methods, simultaneous biaxial stretching by tentering is particularly preferably used. The stretching temperature is in the range of normal temperature to

10 melting point of the polymer gel used, preferably 80 to 140°C and more preferably 100 to 130°C. The draw ratio, on an area basis, is preferably 4 to 400, more preferably 8 to 200 and much more preferably 16 to 100. If the draw ratio is less than 4, the strength of the

15 film is not necessarily sufficient for a separator, whereas if the draw ratio is more than 400, the film can be sometimes hard to stretch and the porosity of the resultant microporous film can sometimes be low.

Plasticizer Removing Step

20 Then, the plasticizer is removed from the stretched film to obtain a microporous polyethylene film. The method for removing the plasticizer is not limited to any specific one. For example, when using paraffin oil or dioctyl phthalate as a plasticizer, it

25 may be extracted with an organic solvent such as methylene chloride or methyl ethyl ketone. And if the resultant microporous film is dried under heat at temperatures lower than or equal to the fusing

temperature, the removal of the plasticizer becomes better. For example, when using a low-boiling compound, such as decaline, as a plasticizer, the plasticizer can be removed only by drying the resultant

5 microporous film under heat at temperatures lower than or equal to the fusing temperature of the microporous film. In either case, to prevent the physical properties of the resultant microporous film from deteriorating due to its shrinkage, it is preferable to

10 remove the plasticizer while placing restrictions on the film, for example, keeping the film in the fixed state. The organic solvent used in the plasticizer removing step can be recycled after completing the plasticizer removing operation by a known method, such

15 as distillation.

To improve the permeability or the dimensional stability, it is also preferable to heat-treat the microporous polyethylene film produced by the above described process at temperatures as high as or

20 lower than the fusing temperature of the film as necessary.

Physical Properties

The microporous polyethylene film obtained from the above described composition not only has

25 mechanical strength and permeability equivalent to those of conventional microporous films, but also secure the high safety of batteries, when used as a battery separator.

The thickness of the microporous film of the present invention is preferably 1 to 500 μm, more preferably 5 to 100 μm and much more preferably 5 to 24 μm. If the thickness of the above described film is

5 smaller than 1 μm, the mechanical strength may not always be sufficient, whereas if the thickness is larger than 500 μm, it may cause interference with the battery size and weight reduction.

The porosity of the microporous film of the

10 present invention is preferably 30 to 70% and more preferably 35 to 50%. If the porosity is lower than 30%, the permeability may not always be sufficient, whereas if the porosity is higher than 70%, sufficient mechanical strength may sometimes not be obtained.

15   The air permeability is preferably 100 to 600 seconds, more preferably 120 to 550 seconds and much more preferably 150 to 500 seconds. If the air permeability is larger than 600 seconds, the permeability may not always be sufficient, whereas if

20 the air permeability is smaller than 100 seconds, the pore diameter can sometimes be too large.

The puncture strength is, from the viewpoint of rupture resistance during the battery winding or inferior battery due to the short circuit between the

25 electrodes, preferably 1 to 20 N/25 μm, more preferably 2 to 18 N/25 μm and particularly preferably 3 to 15 N/25 μm.

The fusing temperature is preferably 140°C or

lower, more preferably 138°C or lower and much more preferably 135°C or lower so as to allow the microporous film to exert a current interrupting effect when the battery is heated due to over charge test or the like.

5   If the fusing temperature is higher than 140°C, the current interruption by the shutdown may be delayed for example at an over charge test or the like, leading to the occurrence of exothermic reaction in the cell.

The film rupture temperature is preferably

10   150°C or higher and more preferably 155°C or higher. If the film rupture temperature is less than 150°C, the film as a separator may rupture at the time of battery test in an oven at 150°C.

The shrinkage force at 150°C is preferably 2N

15   or smaller, more preferably 1.5N or smaller and much more preferably 1.0N or smaller. If the shrinkage force is larger than 2N, since the heat shrinkage force of the battery winding material across the width is large at high temperature, the electrodes may come into

20   contact with each other, thereby causing short-circuit inside the battery.

The shrinkage stress at 150°C is preferably less than 600 kPa, more preferably 300 kPa or smaller, much more preferably 200 kPa or smaller and still much

25   more preferably 150 kPa or smaller.

The reason the microporous polyethylene film obtained from the above described composition can have both fusing properties and heat resistance at the same

time, while maintaining mechanical strength and permeability equivalent to those of conventional microporous films, has not been clarified yet. However, the reason is probably that the high density
5 polyethylene copolymer having a relatively low molecular weight has a low crystalline melting point, while maintaining its high density, and has an effect of lowering the fusing temperature without sacrificing its permeating performance, and besides, since the high
10 density polyethylene copolymer has a high affinity for the high molecular weight component, film rupture, which occurs due to the interface between the components, does not occur during fusing, and the component having a low molecular weight contributes to
15 making it relatively easier to relax the shrinkage force, which is a cause of heat shrinkage.

In the following, the present invention will be described in further detail by several examples. In the following examples and comparative examples, the
20 term "parts" all means "parts by mass".

The testing methods used for testing the characteristics shown in examples and comparative examples are as follows.

(1) Film thickness
25 The film thickness was measured using a dial gauge (OZAKI MFG. CO., LTD.: "PEACOCK No. 25" (trademark)).

(2) Porosity

10 × 10 cm square samples were collected, and

the volume and mass of the samples were measured. Then the porosity was calculated from the following equation using the measured values.

Porosity (%) = (Volume (cm^3) – Mass (g)/Density of

5   polymer composition)/Volume (cm^3) × 100

(3) Puncture strength

The puncture strength test was carried out using "KES-G5 Handy Compression Tester" (trademark), by KATO TECH CO. LTD. under the conditions: probe's tip

10   curvature radius of 0.5 mm and puncture speed of 2 mm/sec. The maximum puncture load (N) was measured.

(4) Air permeability

The air permeability was measured with a Gurley air permeability tester in accordance with JIS

15   P-8117.

(5) Content of comonomer units (Content of α-olefin unit with 3 or more carbon atoms)

The content of comonomer unit (% by mole) was obtained by: dividing the integral value (A), in molar

20   terms, of signal intensity derived from comonomer by the sum of (A) and the integral value (B), in molar terms, of signal intensity derived from ethylene unit; and multiplying the obtained quotient by 100 in the ^{13}C-NMR spectrum.

When using propylene as a comonomer, for example, if the signal intensity of ^{13}C-NMR spectrum derived from the respective carbons in the following structural model are represented by I1, I1', I2, I3,

$I\alpha$, $I\beta$, $I\gamma$, Im and IM,

$$CH_3-CH_2-CH_2-\cdots-(CH_2)_n-CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2-\cdots-CH_2-CH_2-CH_3$$
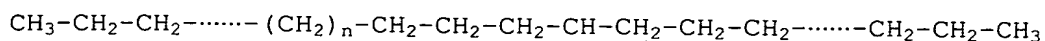
$$1 \quad 2 \quad 3 \quad\quad M \quad \gamma \quad \beta \quad \alpha \quad |m \; \alpha \quad \beta \quad \gamma \quad\quad 3 \quad 2 \quad 1$$

$$CH_3$$

$$1'$$

the following equation holds:

Content of comonomer unit (% by mole) =
$(A)/[(A) + (B)] \times 100$

wherein $(A) = (I1 + Im + I\alpha/2)/3$ and $(B) = (I1 + I2 + I3 + IM + I\alpha/2 + I\beta + I\gamma)/2$.

Since the effect of the terminals is small and therefore can be ignored, if the above described equation is arranged by considering $I1$, $I2$ and $I3$ as Im and $I\alpha$, $I\beta$ and $I\gamma$ as $2Im$, the following equation holds:

Content of comonomer unit (% by mole) =
$Im/[Im + (IM + 5Im)/2] \times 100$

(6) Melt index

The melt index measured at 190°C and a loading of 2.16 kg in accordance with JIS K-7210 was represented by MI.

(7) Fusing temperature/Film rupture (short-circuit) temperature

A schematic view of a measuring device for measuring the fusing temperature is shown in FIG. 1A. Reference numeral 1 denotes a microporous film, reference numerals 2A and 2B denote two sheets of nickel foil having a thickness of 10 μm, and numerals 3A and 3B glass plates. Reference numeral 4 denotes an

electric resistance meter (LCR meter "AG-4311"

(trademark) manufactured by Ando Electric Co., Ltd.),

which is connected to the two sheets of nickel foil 2A

and 2B. Numeral 5 denotes a thermocouple, which is

5   connected to a thermometer 6. Numeral 7 is a data

collector, which is connected to the electric

resistance meter 4 as well as the thermometer 6.

Numeral 8 denotes an oven which is for heating the

microporous film.

10   The measuring device will be described in

further detail. As shown in FIG. 1B, the microporous

film 1 is superimposed to the nickel foil 2A and fixed

thereto lengthwise with "Teflon (trademark)" tape (the

crosshatched portion of the figure). The microporous

15   film 1 is impregnated with 1 mole/liter of lithium

borofluoride solution (solvent: propylene

carbonate/ethylene carbonate/γ-butyl lactone = 1/1/2) as

an electrolyte. As shown in FIG. 1C, "Teflon

(trademark)" tape (the crosshatched portion of the

20   figure) with a 15 mm × 10 mm window portion at its

center is laminated to the nickel foil 2B so that the

nickel foil 2B is masked by the tape with the window

portion left unmasked.

          The two sheets of nickel foil 2A and nickel

25   foil 2B are superimposed so that the microporous film 1

is sandwiched between them, and the two sheets of

nickel foil having been superimposed are then

sandwiched between the glass plates 3A and 3B. At this

point, the window of the nickel foil 2B and the microporous film 1 are placed opposite to each other.

The two glass plates are fixed with a commercially available double clip. The thermocouple 5
5   is fixed to the glass plates with "Teflon (trademark)" tape.

The temperature and electric resistance of the microporous film 1 were continuously measured with the above described measuring device. The temperature
10   was raised from 25°C to 200°C at a raising rate of 2°C/min and the electric resistance was measured with alternating current of 1 kHz. The term "fusing temperature" is defined as the temperature when the electric resistance of the microporous film reaches
15   10^3 Ω. Further, the term "film rupture (short-circuit) temperature" is defined as the temperature when the electric resistance of the microporous film becomes lower than 10^3 Ω again after fusing.

(8) Shrinkage force and stress at the time of
20   fusing

Measurements were made using TMA 50 (trademark) by Shimadzu Corporation. Samples cut to 3 mm width in the TD direction were fixed to chucks so that the distance between the chucks became 10 mm and
25   then set on specialized probes. The initial loading was 0.0098 N (1.0 g) and the probe temperature was raised from 30°C to 200°C at a raising rate of 10°C/min, and the shrinkage force (N) generated was measured.

Further, the shrinkage force (N) when the temperature reached 150°C was measured, and the measured value was used to calculate the shrinkage stress from the following equation:

5   Shrinkage stress (kPa) = [shrinkage force (150°C)/(3 × T)] × 100 × 9.807 × 10000

wherein T represents the thickness of a sample (μm).

(9) Viscosity average molecular weight

Measurements were made in accordance with
10 ASTM-D4020. The microporous film was dissolved in a decaline solution at 135°C, the intrinsic viscosity [η] was measured, and the viscosity average molecular weight (Mv) was calculated from the following equation.

$$[\eta] = 6.77 \times 10^{-4} \; Mv^{0.67}$$

15   (10) GPC

Measurements were made using 150C ALC/GPC (trademark) by Waters Corporation under the following conditions, and a calibration curve was prepared using standard polystyrene. A molecular weight distribution
20 curve in polystyrene terms was obtained by multiplying each of the molecular weight components by 0.43 (Q factor of polyethylene/Q factor of polystyrene = 17.7/41.3). The molecular weight of the unfused matter was calculated by measuring the weight.

25   Column: two columns of GMH6-HT (trademark) + two columns of GMH6-HTL (trademark) by TOSOH CORPORATION

Mobile phase: o-diclorobenzene

Detector: differential refractometer

Flow rate: 1.0 ml/min

Column temperature: 140°C

Sample concentration: 0.05 wt%

5   (11) Battery evaluation

Preparation of positive electrode

A slurry was prepared by dispersing in N-methylpyrrolidone (NMP) 92.2% by weight of lithium cobalt composite oxide $LiCoO_2$ as an active material,

10   2.3% by weight of flake graphite and of acetylene black as conductive materials, and 3.2% by weight of polyvinylidene fluoride (PVDF) as a binder. The slurry was coated on one side of aluminium foil 20 μm thick, which was to be a positive electrode current collector,

15   with a die coater, dried at 130°C for 3 minutes, and compression molded with a roll pressing machine. The coating was performed so that the amount of the positive electrode active material coated was 250 g/m^2 and the bulk density of the active material was 3.00

20   g/cm^3. The resultant positive electrode was cut to about 40 mm wide to take the form of a strip.

Preparation of negative electrode

A slurry was prepared by dispersing in purified water 96.9% by weight of synthetic graphite as

25   an active material and 1.4% by weight of ammonium salt of carboxymethylcellulose and 1.7% by weight of styrene-butadiene copolymer latex as binders. The slurry was coated on one side of copper foil 12 μm

thick, which was to be a negative electrode current
collector, with a die coater, dried at 120°C for 3
minutes, and compression molded with a roll pressing
machine. The coating was performed so that the amount

5 of the negative electrode active material coated was
106 g/m^2 and the bulk density of the active material was
1.35 g/cm^3. The resultant negative electrode was cut to
about 40 mm wide to take the form of a strip.

Preparation of non-aqueous electrolyte

10 A non-aqueous electrolyte was prepared by
dissolving LiPF$_6$ as a solute in a mixed solvent of
ethylene carbonate/ethyl methyl carbonate = 1/2 (volume
ratio) so that the concentration of LiPF$_6$ was 1.0
mole/liter.

15 Battery assembly

The above described microporous film
separators, strip positive electrode and strip negative
electrode were superimposed in the order of strip
negative electrode, separator, strip positive electrode

20 and separator and then wound more than one time into a
swirl to prepare an electrode laminate. The electrode
laminate was pressed into a flat sheet and packed in an
aluminum container. The aluminum lead drawn out from
the positive electrode current collector was connected

25 to the container wall, while the nickel lead drawn out
from the negative electrode current collector being
connected to the terminal on the container lid. Then,
the above described non-aqueous electrolyte was poured

into the container. The lithium ion battery thus produced was 6.3 mm thick, 30 mm wide and 48 mm high and designed to have a nominal service capacity of 620 mAh.

5   The battery was first charged at a current of 310 mAh (0.5 C) to a battery voltage of 4.2 V in the atmosphere at 25°C and continued to be charged for totaling 6 hours in such a manner as to throttle the current flow from 310 mAh while keeping the battery

10 voltage at 4.2 V. To conduct an over charge test for this battery, the battery was charged at a current of 620 mAh (1.0 C) to a battery voltage (the maximum charged voltage) of 10 V. The degree of exothermic reaction occurring in this state was observed.

15 Example 1

First, 10.5 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95), 10.5 parts of high

20 density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95), 5.2 parts of high density homopolyethylene having an Mv of 700000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of

25 0.95), 8.8 parts of ultrahigh molecular weight homopolyethylene having an Mv of 2000000 (comonomer unit content of 0.0% by mole, density of 0.94), and 0.3 parts of tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-

hydroxyphenyl)propionate]methane as an antioxidant were blended and fed to a twin screw extruder through a feeder. Then, 65 parts of liquid paraffin (P-350 (trademark) manufactured by Matsumura Oil Co., Ltd.)

5 was poured into the extruder through a side feed, the blend was kneaded at 200°C, and the kneaded blend was extruded from a T die fixed to the tip of the extruder, followed by cool solidification with a cast roll having been cooled to 25°C to form a gel sheet 1200 μm thick.

10 The gel sheet was stretched at 120°C to 7- × 7-fold size with a simultaneous biaxial stretching machine, and the stretched film was immersed in methyl ethyl ketone to extract and remove the liquid paraffin and dried to obtain a microporous film. The obtained microporous

15 film was heat fixed at 125°C. The physical properties of the obtained film are shown in Table 1. The molecular weight components calculated from the measurements of the film by GPC were as follows: the component having a molecular weight of 1000000 or more

20 was 7% and the component having a molecular weight of 10000 or less was 5%.

Example 2

A microporous film was produced in the same manner as in example 1, provided that the polyethylene

25 materials used were 10.5 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95), 14 parts of high

density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of ultrahigh molecular weight polyethylene having an Mv of 2000000 (MI of less than

5   0.01) (comonomer unit content of 0.0% by mole, density of 0.94) and the thickness of the gel sheet was 1400 μm.

The physical properties of the obtained microporous film are shown in Table 1.

10 Example 3

A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 7 parts of a high density polyethylene copolymer having an MI of 1.0 (Mv of

15 120000) (comonomer: propylene, propylene unit content of 0.8% by mole, density of 0.94), 17.5 parts of high density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of ultrahigh molecular weight

20 homopolyethylene having an Mv of 2000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.94) and the thickness of the gel sheet was 1000 μm.

The physical properties of the obtained

25 microporous film are shown in Table 1.

Example 4

A microporous film was produced in the same manner as in example 1, provided that the polyethylene

materials used were 14 parts of a high density
polyethylene copolymer having an MI of 0.8 (Mv of
150000) (comonomer: propylene, propylene unit content
of 0.6% by mole, density of 0.95) and 21 parts of high

5   density homopolyethylene having an Mv of 700000 (MI of
less than 0.01) (comonomer unit content of 0.0% by
mole, density of 0.95). The physical properties of the
obtained microporous film are shown in Table 1.

Example 5

10   A microporous film was produced in the same
manner as in example 1, provided that the polyethylene
materials used were 10.5 parts of a high density
polyethylene copolymer having an MI of 2.0 (Mv of
100000) (comonomer: propylene, propylene unit content

15   of 0.4% by mole, density of 0.95), 14 parts of high
density homopolyethylene having an Mv of 300000 (MI of
0.05) (comonomer unit content of 0.0% by mole, density
of 0.95) and 10.5 parts of ultrahigh molecular weight
polyethylene having an Mv of 2000000 (MI of less than

20   0.01) (comonomer unit content of 0.0% by mole, density
of 0.94). The physical properties of the obtained
microporous film are shown in Table 1.

Example 6

             A microporous film was produced in the same

25   manner as in example 1, provided that the polyethylene
materials used were 26.3 parts of a high density
polyethylene copolymer having an MI of 0.8 (Mv of
150000) (comonomer: propylene, propylene unit content

of 0.6% by mole, density of 0.95) and 8.8 parts of
ultrahigh molecular weight polyethylene having an Mv of
3000000 (MI of less than 0.01) (comonomer unit content
of 0.0% by mole, density of 0.93, average particle size
5   of 35 μm).   The physical properties of the obtained
microporous film are shown in Table 1.   The molecular
weight components calculated from the measurements of
the film by GPC were as follows: the component having a
molecular weight of 1000000 or more was 7% and the
10   component having a molecular weight of 10000 or less
was 7%.

Example 7

A microporous film was produced in the same
manner as in example 1, provided that the polyethylene
15   materials used were 29.8 parts of a high density
polyethylene copolymer having an MI of 0.8 (Mv of
150000) (comonomer: propylene, propylene unit content
of 0.6% by mole, density of 0.95) and 5.3 parts of
ultrahigh molecular weight polyethylene having an Mv of
20   4500000 (MI of less than 0.01) (comonomer unit content
of 0.0% by mole, density of 0.93, average particle size
of 60 μm).   The physical properties of the obtained
microporous film are shown in Table 1.

Example 8

25   A microporous film was produced in the same
manner as in example 1, provided that the stretching
temperature was 117°C.   The physical properties of the
obtained microporous film are shown in Table 1.

Example 9

A microporous film was produced in the same manner as in example 1, provided that the thickness of the gel sheet was 900 μm and the stretching temperature was 115°C. The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 1

A microporous film was produced in the same manner as in example 1, provided that the polyethylene material used was 35 parts of high density homopolyethylene having an Mv of 700000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 2

A microporous film was produced in the same manner as in example 1, provided that the polyethylene material used was 35 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 3

A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 10.5 parts of copolymerized low density polyethylene having an MI of 0.3 (Mv of 170000)

(comonomer: butene, butene unit content of 1.8% by mole, density of 0.92), 14 parts of high density homopolyethylene having a viscosity average molecular weight of 300000 (MI of 0.05) (comonomer unit content

5 of 0.0% by mole, density of 0.95) and 10.5 parts of high density homopolyethylene having an Mv of 2000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

10 Comparative Example 4

A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 10.5 parts of high density homopolyethylene having an Mv of 150000 (MI of 0.8)

15 (comonomer unit content of 0.0% by mole, density of 0.97), 14 parts of high density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of ultrahigh molecular weight polyethylene having an Mv of

20 2000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 5

25 A microporous film was produced in the same manner as in example 1, provided that 9 parts of polyethylene copolymer having an MI of 3.0 (Mv of 70000, melting point of 127°C, hexane unit content of

1.3% by mole, density of 0.94) and 36 parts of high density homopolyethylene having an Mv of 280000, and 55 parts of liquid paraffin were used. The physical properties of the obtained microporous film are shown

5 in Table 1.

Comparative Example 6

A microporous film was produced in the same manner as in example 1, provided that 17.1 parts of copolymerized linear high density polyethylene having

10 an MI of 0.8 (Mv of 120000) (comonomer: propylene, propylene unit content of 1.3% by mole, density of 0.94), 15.2 parts of high density homopolyethylene having an Mv of 600000 and 5.7 parts of high density homopolyethylene having an Mv of 100000, as

15 polyethylene materials, and 62 parts of liquid paraffin were used. The physical properties of the obtained microporous film are shown in Table 1.

Table 1

Composition		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Copolymerized linear high density PE1	MI0.8, comonomer 0.6%	30	30	-	40	-	75	85	30	30
Copolymerized linear high density PE2	MI1.0, comonomer 0.8%	-	-	20	-	-	-	-	-	-
Copolymerized linear high density PE3	MI2.0, comonomer 0.4%	-	-	-	-	30	-	-	-	-
Copolymerized linear high density PE4	MI3.0, comonomer 1.3%	-	-	-	-	-	-	-	-	-
Copolymerized linear high density PE5	MI0.8, comonomer 1.3%	-	-	-	-	-	-	-	-	-
Copolymerized linear low density PE	MI0.3, comonomer 01.3%	-	-	-	-	-	-	-	-	-
High density PE1	100000	-	-	-	-	-	-	-	-	-
High density PE2	150000	-	-	-	-	-	-	-	-	-
High density PE3	300000	30	40	50	-	40	-	-	30	30
High density PE4	600000	-	-	-	-	-	-	-	-	-
High density PE5	700000	15	-	-	60	-	-	-	15	15
Ultrahigh molecular weight PE1	2000000	25	30	30	-	30	-	-	25	25
Ultrahigh molecular weight PE2	3000000	-	-	-	-	-	25	-	-	-
Ultrahigh molecular weight PE3	4500000	-	-	-	-	-	-	15	-	-

Table 1 (Cont'd)

Composition		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Copolymerized linear high density PE1	MI0.8, comonomer 0.6%	–	100	–	–	–	–
Copolymerized linear high density PE2	MI1.0, comonomer 0.8%	–	–	–	–	–	–
Copolymerized linear high density PE3	MI2.0, comonomer 0.4%	–	–	–	–	–	–
Copolymerized linear high density PE4	MI3.0, comonomer 1.3%	–	–	–	–	20	–
Copolymerized linear high density PE5	MI0.8, comonomer 1.3%	–	–	–	–	–	15
Copolymerized linear low density PE	MI0.3, comonomer 01.3%	–	–	30	–	–	–
High density PE1	100000	–	–	–	–	–	–
High density PE2	150000	–	–	–	30	–	45
High density PE3	300000	–	–	40	40	–	–
High density PE4	600000	–	–	–	–	80	40
High density PE5	700000	100	–	–	–	–	–
Ultrahigh molecular weight PE1	2000000	–	–	30	30	–	–
Ultrahigh molecular weight PE2	3000000	–	–	–	–	–	–
Ultrahigh molecular weight PE3	4500000	–	–	–	–	–	–

Table 1 (cont'd)

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Film characteristics	Film Mv (10000 unit)	50	52	48	40	45	48	43	50	50
	Film comonomer (mole %)	0.2	0.2	0.5	0.3	0.1	0.5	0.6	0.2	0.2
	Film thickness (μm)	17	20	12	17	17	17	17	17	8
	Porosity (%)	40	42	38	40	40	42	43	40	40
	Air permeability (sec)	400	450	280	390	500	480	470	400	200
	Puncture strength (N)	5.1	6	4.5	5.4	5	4.7	4.6	6	4.5
	Fusing temperature (°C)	137	137	135	135	135	132	130	137	137
	Film rupture temperature (°C)	157	155	155	151	154	155	155	156	156
	Shrinkage force (150°C) (N)	0.50	0.60	0.35	0.46	0.45	0.46	0.45	0.92	1.9
	Shrinkage stress (150°C) (kPa)	99	100	98	90	89	90	88	180	800
	Battery evaluation	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred

Table 1 (cont'd)

Film Characteristics			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
	Film Mv	10000 unit	55	12	50	50	25	30
	Film comonomer	mole %	0	0.6	0.6	0	0.7	0.2
	Film thickness	μm	17	21	18	18	25	20
	Porosity	%	40	45	36	41	40	41
	Air permeability	sec	370	490	650	390	610	430
	Puncture strength	N	5.1	3.4	4.1	4.5	5	4.9
	Fusing temperature	°C	141	132	134	139	130	131
	Film rupture temperature	°C	151	140	145	150	142	145
	Shrinkage force (150°C)	N	1.0	Membrane ruptured	Membrane ruptured	Membrane ruptured	Membrane ruptured	Membrane ruptured
	Shrinkage stress (150°C)	kPa	200	-	-	-	-	-
	Battery evaluation		exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred

INDUSTRIAL APPLICABILITY

The microporous film of the present invention can be suitably used in the fields of, for example, microfiltration films, battery separators, condenser

5 separators and fuel cell materials.